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Microwave spectrum and quadrupole coupling constants of 3-chloropyridine

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The microwave spectrum of 3-chloropyridine has been studied in the 22.0-25.5 GHz and 28.5-40.0 GHz frequency range. The rotattional constants and the quadrupole coupling constants for the Cl^{35} species are : $A = 5839.652 \pm 0.015$ MHz, $B = 1604.392 \pm 0.007$ MHz, $C = 1258.531 \pm 0.007$ MHz and $\chi_{aa} = -71.58 \pm 1.02$ MHz, $\chi_{bb} = 37.63 \pm 1.45$ MHz, $\chi_{cc} = 33.95 \pm 1.02$ MHz; for the Cl^{37} sepcies $A = 5839.575 \pm 0.024$ MHz, $B = 1558.825 \pm 0.005$ MHz, $C = 1230.299 \pm 0.005$ MHz and $\chi_{aa} = -57.35 \pm 0.95$ MHz, $\chi_{bb} = 31.11 \pm 1.34$ MHz, $\chi_{cc} = 26.24 \pm 0.95$ MHz.

1. INTRODUCTION

The study of the microwave spectra of peripherally substituted ring compounds is one of contemporaneous interest. These studies yield information on the influence of such substitutions on the geometry of rings. Present day literature evidences a considerable amount of activity having been channelized in this field (Bak *et al* 1962, Rosenthal *et al* 1965, Nygaard *et al* 1968, Sharma *et al* 1971, Scappini *et al* 1972, Michel *et al* 1974).

The present work on 3-chloropyridine was undertaken with such an end in view though, really, a complete structural determination would be necessary before any quantitative estimates of the influence on the pyridine ring by substitution of a chlorine atom in the meta position could be made.

This paper presents details of a work whose essential results have been communicated in a short note earlier (Chatterjee *et al* 1974). At the time of completion of this work we came to learn that Sharma *et al* (private communication) have also completed work on the Cl^{35} species of the molecule. Their rotational and quadrupole coupling constants agree very nearly with those reported by us here.

2. EXPERIMENTAL

A conventional 100 kHz Stark modulated microwave spectrometer built in our laboratory was used for the study of this molecule in the frequency range 22.0-25.5 GHz. Recorded spectra were used during the preliminary stages of

the assignment of spectral lines These records were provided with frequency markers spaced 25 0 MHz apart In the final stages of the analysis oscilloscope display of spectral lines was resorted to.

Accurate frequency measurements were made using a microwave frequency standard driven by a GR 1100 AP Primary Frequency Standard at 100 kHz (Banerjee *et al* 1969) Standard frequency markers obtained from the microwave frequency standard were superimposed on absorption line peaks displayed on an oscilloscope The measurements were made for frequency sweeps over the line both in the forward and backward direction and the final value of the absorption frequency was taken as the mean of these measurements

The sample of 3-chloropyridine was obtained from M/s. Koch Light & Co and was used without further purification All measurements were made at room temperature using pressures between 10^{-2} and 10^{-3} mm of Hg.

The spectrum was rich in lines and many of them showed hyperfine splitting which could be attributed to the chlorine nucleus. The quadrupole interaction of the nitrogen nucleus being of a second order in comparison with that of the chlorine nucleus was not included in the analysis of the quadrupolar coupling constants Although many lines have been assigned, many have been left over and are thought of as appearing due to excited states or J states higher than the maximum used in this analysis

Through the courtesy of Dr A. C Legon of the University College, London, we had at our disposal rapid scan recordings of the spectra in the 28.5—40 0 GHz range for four different Stark fields. He also provided us with a more detailed recorded scan of the 30.0-31 0 GHz range at a single Stark field. These records were all run at room temperature at a pressure of 50 μ on a H.P. Microwave Spectrometer. The data provided by these records have also been used in our analysis and are presented in this paper

The rapid scan records have frequency markers spaced 100 MHz apart and the average distance on the chart paper between two such markers is about 42 mm. Absorption line frequencies measured by linear interpolation is believed to be accurate to $\pm$2.5 MHz. In the case of the detailed scan over 30.0-31.0 GHz, the frequency markers are spaced 10 MHz apart and the corresponding distance between two such markers is again about 42 mm Absorption line frequencies measured by linear interpolation is believed to be accurate to $\pm$ 0.2 MHz and in the case of hyperfine splittings when they are present, the difference frequency is better than 0 1 MHz. Difference frequencies measured for quadrupolar splittings for transitions assigned in the 30.0 –31 0 GHz range have been used in the least square analysis for determining the hyperfine coupling constants whereas in the case of the least square analysis for determination of the rotational constants only transitions assigned in the 22 0 - 25 5 GHz range have been used

3 Analysis and Results

The structural determinations of pyridine by Bak *et al* (1958) provide a good starting point for the model for 3-chlorpyridine. Combining with this the results of Poynter (1963) for chlorobenzene, one has a reasonable C-Cl bond length as well as quadrupole coupling constants for the Cl nucleus. Using these results we generated an expected pattern for the spectrum of 3-chloropyridine in the 22.0-40.0 GHz frequency range. Since *a* and *b* types of transitions for both Cl^{35} and Cl^{37} species were expected, the generated spectrum was naturally found to be rich in lines and this was amply corroborated by the actual spectrum of the molecule.

To begin with, the first step was to try and assign the *Q*-branch lines for the Cl^{35} species. The procedure adopted was one of *zeroing in* onto the $(A-C)/2$ and κ values starting from assignments of high J *Q*-branch lines and gradually converging in to low J lines. It was noted that one should expect a number of very strong *Q*-branch lines running from $J = 20$ to $J = 39$ in the 28.5-40.0 GHz range. After a few attempts we were able to identify almost all these strong lines. The frequencies of these lines were then used in a least square analysis for evaluating $(A-C)/2$ and κ. The values obtained for these parameters were then used for predicting lower J *Q*-branch transition frequencies and the search for lines in the vicinity of these predicted frequencies was repeated. The process was repeated till a sufficiently large number of low J *Q*-branch lines had been identified and fairly good estimates for $(A-C)/2$ and κ obtained.

At this stage we began the search for low J *R*-branch lines. Here, at every step, we adopted a least square fitting technique for including only those lines which gave a standard deviation well within the errors of frequency measurements. It might be mentioned that none of the lines were identified by the Stark effect.

The analysis of the spectrum of the Cl^{37} species was carried out in an identical manner.

As regards evaluation of the hyperfine coupling constants, since we had, a priori, a knowledge of the transitions which were expected to exhibit splittings and an approximate estimate of such splittings, it was not difficult to identify them. After making measurements of these splittings for a sufficient number of transitions the hyperfine coupling constants for both varieties of the quadrupolar nuclei were evaluated using a least square analysis. For those lines which were split quadrupolar corrections were made in order to arrive at the hypothetical rigid rotor positions before including these transitions in the least square analysis for evaluating the rotational constants.

Using the evaluated rotational and quadrupolar coupling constants given in table 5, the calculated spectra along with the experimentally observed frequencies for Cl^{35} and Cl^{37} are given in tables 1 and 2 respectively.

Table 1. Observed and calculated transitions of Cl^{35} 3-chloropyridine. frequencies are given in MHz

$J\kappa_1,\kappa_1$ - $J'\kappa_1',\kappa_1'$	F - F'	Obs. freq.*	Calc. freq.
$7_{1,6}$—$7_{2,6}^{a}$	17/2—17/2	22678 43	22678.937
	15/2—15/2	22682.65	22683.492
	13/2—13/2	22681 55	22682 505
	11/2 11/2	22679.65	22678 010
$7_{4,4}$ - $7_{3,4}^{b}$	17/2- -17/2	30604 50	30604.262
	15/2—15/2	30611 44	30611.097
	13/2— 13/2	30610 15	30609.705
	11/2 - 11/2	30603.21	30602.870
$8_{1,7}$- - $7_{1}^{a}{}_{,6}$	19/2—17/2		23786.216
	17/2- 15/2		23786 117
		23786.04	
	15/2— 13/2		23785 713
	13/2- - 11/2		23785 811
$8_{1,7}$—$7_{2,6}$	19/2 - -17/2		22658 201
		22658.50	
	17/2- - 15/2		22658 001
	15/2 - 13/2		22657 397
		— —	
	13/2— 11/2		22657 197
$8_{2,6}$—$7_{2,5}$	19/2—17/2		23970 599
		23971 42	
	17/2 15/2		23970.399
	15/2 13/2		23969 687
	13/2—11/2		23969 487
$8_{3,5}$ $7_{3,4}$	19/2 17/2		23242 101
		23242 23	
	17/2—15/2		23242 224
	15/2—-13/2		23240 106
		—	
	13/2 - -11/2		23240 229
$8_{3,6}$ $8_{2}^{a}{}_{,7}$	19/2 19/2	23084 35	23084 053
	17/2 - 17/2	23087.45	23087 487
	15/2—15/2	23086.96	23086.872
	13/2- - 13/2	23083 85	23083 438
$8_{4,4}$ - - $8_{3}^{b}{}_{,5}$	19/2 19/2	30414 28	30414 210
	17/2- -17/2	30419.73	30419.605
	15/2 - -15/2	30418 77	30418.640
	13/2—13/2	30413 32	30413 244
$9_{0,9}$—$8_{0,8}$	21/2 19/2		24069 908
	19/2—17/2		24069.989
		24070 45	
	17/2— 15/2		24069 649
	15/2— 13/2		24069 567
$9_{1,8}$- $8_{0,8}$	21/2—19/2		24749 919
	19/2—17/2		24750.329
		24749 41	
	17/2—15/2		24749.936
	15/2—13/2		24749.526

Table 1 (contd.)

$J\kappa_1,\kappa_1 - J'\kappa_1',\kappa_1'$	F—F'	Obs freq.*	Calc. freq
$9_{1,9}$—$8_{1,8}{}^a$	21/2—19/2		23772 983
	19/2—17/2	23773 00	23772 875
	17/2—15/2		23772.575
	15/2—13/2		23772 683
$9_{3,7}$—$9_{3,6}{}^a$	21/2—21/2	23632 26	23632.336
	15/2—15/2		23631.918
	19/2—19/2	23635.10	23634.974
	17/2—17/2		23634 554
$9_{4,5}$—$9_{3,6}{}^b$	21/2—21/2	30114.73	30114 680
	15/2—15/2		30113.975
	19/2—19/2	30119.11	30119.094
	17/2—17/2		30118 389
$10_{1,9}$ - $9_{2,8}{}^a$	23/2—21/2	22839 87	22840.228
	17/2—15/2		22840 264
	21/2—19/2	22838 37	22838.338
	19/2—17/2		22838 374
$10_{2,9}$— $10_{1,10}{}^a$	23/2—23/2	23146 31	23146 537
	17/2- 17/2		23146.395
	21/2—21/2	23147 67	23147.521
	19/2—19/2		23147 379
$10_{3,8}$—$10_{2,9}{}^a$	23/2—23/2	24341 77	24341.749
	17/2—17/2		24341.455
	21/2 21/2	24344 06	24343.794
	19/2—19/2		24343.499
$10_{4,7}$—$10_{3,8}{}^b$	23/2—23/2	30768 96	30768 876
	17/2—17/2		30768.390
	21/2—21/2	30772.40	30772.246
	19/2—19/2		30771 760
$11_{2,10}$— $11_{1,11}{}^a$	25/2— 25/2	25090 70	25090.692
	19/2—19/2		25090.591
	23/2—23/2	25091 70	25091.458
	21/2—21/2		25091.357
$11_{3,9}$—$11_{2,10}{}^a$	25/2—25/2	25226.10	25226.109
	19/2—19/2		25225.900
	23/2—23/2	25227.90	25227.705
	21/2—21/2		25227.495

Table 1 (contd)

$J_{K_-,K_1} - J'_{K_{-1},K'_1}$	$F'—F''$	Obs freq *	Calc freq.
$11_{4,8} - 11_{3,9}$[b]	25/2 – 25/2	30858 17	30858.213
	19/2—19/2		30857.850
	23/2 23/2	30860.87	30860 976
	21/2—21/2		30860 613
$12_{1,11}—12_{0,12}$[a]	27/2 – 27/2	24111 49	24111.667
	25/2 – 25/2		24111.477
	23/2– 23/2		24111 500
	21/2 21/2		24111.690
$15_{2,16}— 15_{1,14}$[a]	33/2– 33/2	23119 55	23120.016
	31/2- 31/2		23119 543
	29/2– 29/2		23119 589
	27/2—27/2		23120.062
$15_{4,11}$ $15_{3,12}$[a]	33/2—33/2	25005 92	25006 223
	27/2– 27/2		25006 038
	31/2—31/2	25007 91	25008 136
	29/2 29/2		25007.950
$16_{4,13}— 16_{3,13}$[a]	35/2—35/2	23911 91	23912 175
	29/2- 29/2		23912 027
	33/2—33/2	23913.12	23913 791
	31/2 31/2		23913 643

* ⊥ 0 2 MHz

[a] Transitions included in least square analysis for evaluating rotational constants

[b] Transitions included in least square analysis for evaluating quadrupole coupling constants

Table 2 Observed and calculated transitions of Cl^{37} 3-chloropyridine Frequencies are given in MHz

$J_{\kappa_1,\kappa_1} - J'_{\kappa'_1,\kappa_1'}$	$F - F'$	Obs. freq.*	Calc. freq.
$7_{4,3} - 7_3{}^b{}_{,4}$	17/2—17/2	30892 60	30892 723
	15/2—15/2		30898.216
	13/2 13/2	30897.04	30897 097
	11/2—11/2	30891.49	30891 605
$8_{1,7} - 7_1{}^a{}_{,6}$	19/2—17/2	—	23183 585
	17/2—15/2		23183 521
	15/2 13/2	23183.45	23183 190
	13/2 - 11/1	—	23183 253
$8_{3,6} - 8_2{}^{a,b}{}_{,7}$	19/2 - 19/2	23166 39	23166 509
	13/2—13/2		23166 027
	17/2 — 17/2	23169.03	23169 207
	15/2—15/2		23168.724
$8_{1,1} - 8_3{}^b{}_{,5}$	19/2- 19/2	30726 74	30726 619
	17/2 17/2	30731 14	30730 963
	15/2 15/2	—	30730.186
	13/2—13/2	30725 97	30725 841
$9_{0,9} - 8_0{}^a{}_{,8}$	21/2— 19/2		23539 127
	19/2 —17/2	23539.05	23539 226
	17/2 —15/2		23538 951
	15/2—13/2		23538 852
$9_{1,9} - 8_1{}^a{}_{,8}$	21/2—19/2		23226.194
	19/2—17/2	23225 92	23226 117
	17/2 - 15/2		23225 881
	15/2— 13/2		23225 957
$9_{2,8} - 8_2{}^a{}_{,7}$	21/2—19/2		24780 458
	19/2—17/2	24780 11	24780.032
	17/2—15/2		24779 872
	15/2—13/2		24780 298
$9_{4,5} - 8_4{}^a{}_{,5}$	21/2—19/2	25272 02	25271 856
	15/2—13/2		25272.070
	19/2—17/2	25270.32	25269 922
	17/2—15/2		25270.137
$9_{3,7} - 9_2{}^{a,b}{}_{,8}$	21/2—21/2	23664 15	23664.360
	15/2—15/2		23664 033
	19/2—19/2	23666 10	23666.405
	17/2—17/2		23666.079
$10_{2,8} - 10_1{}^a{}_{,10}$	23/2 —23/2	22758 55	22758.741
	17/2—17/2		22758.664
	21/2 - 21/2	22759 67	22759.274
	19/2—19/2		22759 197

Table 2 (contd.)

$J_{K_1,K_1}-J'_{K_1,K_1'}$	$F-F'$	Obs. freq.*	Calc freq.
$10_{3,9}-10_2{}^{a,b}{}_{,9}$	23/2—23/2		24310 790
		24310.99	
	17/2—17/2		24310.565
	21/2—21/2		24312.349
		24312 63	
	19/2—19/2		23312.124
$10_{4,6}-10_3{}^{b}{}_{,7}$	23/2 —23/2		30074.402
		30073 96	
	17/2— 17/2		30073.966
	21/2— 21/2		30077 426
		30076.86	
	19/2—19/2		30076.990
$11_{2,10}-10_{2,9}$	25/2—23/2		30081.785
	23/2—21/2		30081 583
		30080.83	
	21/2 19/2		30081 451
	19/2—17/2		30081.652
$11_{2,10}-11_1{}^{a}{}_{,11}$	25/2—25/2		24615 082
		24615.30	
	19/2- 19/2		24615.035
	23/2— 23/2		24615 442
		24615 97	
	21/2—21/2		24615 395
$11_{3,9}-11_2{}^{a}{}_{,10}$	25/2—25/2		25119.712
		25119.91	
	19/2—19/2		25119 556
	23/2 —23/2		25120 899
		—	
	21/2—21/2		25120 743
$12_{1,11}-12_{0,12}$	27/2—27/2		23217 873
	25/2— 25/2		23217 338
		23217.05	
	23/2—23/2		23217 403
	21/2—21/2		23217 937
$14_{2,13}-14_{1,14}$	31/2—31/2		30883 324
	29/2 —29/2		30883 417
		30883.96	
	27/2—27/2		30883 407
	25/2- -25/2		30883.315
$15_{2,13}-15_{1,14}$	33/2—33/2		21997.043
	31/2—31/2		21996 415
		21995 95	
	29/2—29/2		21996.476
	27/2—27/2		21997 105
$15_{3,13}-15_{2,14}$	33/2—33/2		30105.350
	31/2—31/2		30105 689
		30105.44	
	29/2- -29/2		30105.656
	27/2- 27/2		30105.317
$16_{2,11}-16_{1,15}$	35/2- 35/2		24868.447
	33/2—33/2		24867.805
		24867.10	
	31/2—31/2		25867 864
	29/2—29/2		24868 505

*$\pm$0.2 MHz

[a]Transitions included in least square analysis for evaluating rotational constants

[b]Transitions included in least square analysis for evaluating quadrupole coupling constants

Tables 3 and 4 give a list of some high J Q-branch assignments for Cl^{35} and Cl^{37} respectively. Since the observed frequencies of Tables 3 and 4 are accurate to ± 2.5 MHz, no centrifugal distortion analysis was attempted

Table 3. Observed and calculated frequencies of some high J Q- branch transitions of Cl^{35} 3-chloropyridine. Frequencies are given in MHz

Transition $J_{K_1,K_1} - J_{K_1',K_1'}$	Obs. freq.*	Calc freq
$20_{2,18} - 20_{1,19}$	38641 0	38642 1
$20_{4,17} - 20_{3,18}$	37655 5	37660.4
$20_{5,15} - 20_{4,16}$	31953 4	31951.2
$21_{5,16} - 21_{2,19}$	30434 4	30436 3
$21_{1,18} - 21_{5,17}$	39306 5	39308 3
$21_{5,16} - 21_{4,17}$	30515 4	30520 0
$22_{3,19} - 22_{2,20}$	33741.7	33744 1
$22_{5,17} - 22_{4,18}$	29211 4	20214 2
$23_{1,20} - 23_{2,21}$	37131 8	37135.2
$25_{4,21} - 25_{3,22}$	31096.0	31101 7
$25_{0,19} - 25_{5,20}$	39037 6	39037 7
$26_{1,22} - 26_{0,23}$	34247 5	34252 3
$26_{0,20} - 26_{5,21}$	37315 7	37316 3
$27_{4,23} - 27_{3,24}$	37668 2	37673 0
$27_{5,21} - 27_{0,22}$	35659 3	35660.7
$28_{5,23} - 28_{4,24}$	29916 0	29923 7
$28_{6,22} - 28_{5,23}$	34200 0	34203 7
$29_{5,24} - 29_{1,28}$	31996 3	32002.8
$29_{6,23} - 29_{5,24}$	33073 5	33077 3
$30_{5,25} - 30_{4,26}$	34620 4	34629.0
$30_{6,24} - 30_{5,25}$	32396.3	32398 9
$31_{7,26} - 31_{4,27}$	37715 1	37725 2
$31_{6,25} - 31_{5,26}$	32259 3	32262 5
$32_{6,26} - 32_{5,27}$	32727 2	32734.5
$33_{6,27} - 33_{5,29}$	33843.2	33852 3
$34_{6,28} - 34_{5,29}$	35611 1	35621.8
$34_{7,27} - 34_{6,29}$	38956.8	38959.5
$35_{6,29} - 35_{5,30}$	38002.8	38015.5
$35_{7,28} - 35_{6,29}$	37814 5	37819 9
$36_{7,29} - 36_{6,30}$	37200 0	37209 3
$37_{7,30} - 37_{6,31}$	37208 3	37217 0
$38_{7,31} - 38_{6,32}$	37888 9	37901.0
$39_{7,32} - 39_{6,33}$	39274.1	39286 8

* ± 2.5 MHz

Table 4. Observed and calculated frequencies of some high J Q-branch transitions of Cl^{37} 3-chloropyridine. Frequencies are given in MHZ

Transition $J\kappa_1,\kappa_1 - J\kappa_1',\kappa_1'$	Obs freq.	Calc.freq
$20_{4,17} - 20_{3,18}$	37070 4	37071 1
$20_{5,16} - 20_{4,16}$	33090 7	33093 8
$21_{3,18} - 21_{2,19}$	28689.8	28689 4
$21_{5,16} - 21_{4,17}$	31679 6	31677.1
$23_{3,20} - 23_{2,21}$	35094.1	35094 7
$23_{5,18} - 23_{4,19}$	29095 4	29097 3
$25_{1,21} - 25_{3,22}$	29247 2	29249 7
$26_{4,22} - 26_{3,23}$	32062 3	32061 1
$28_{5,23} - 28_{4,24}$	28893 8	28896 7
$28_{6,22} - 28_{5,23}$	35697.5	35699 5
$29_{5,24} - 29_{4,25}$	30440 1	30445 0
$29_{6,24} - 29_{5,24}$	34311 7	34316 1
$30_{5,25} - 30_{4,26}$	32544 7	32550 5
$30_{6,24} - 30_{5,25}$	33259 9	33264 3
$31_{5,26} - 31_{4,27}$	35164.2	35169 0
$31_{6,25} - 31_{5,26}$	32644 1	32649 1
$32_{5,27} - 32_{4,28}$	38220.7	38226.3
$32_{6,26} - 32_{5,27}$	32549 4	32555 2
$33_{6,27} - 33_{5,28}$	33036 1	33042 0
$34_{6,28} - 34_{5,29}$	34137 0	34142 7
$35_{6,29} - 35_{5,30}$	35855.9	35862.7
$35_{7,28} - 35_{6,29}$	39340 1	39344.0
$36_{6,30} - 36_{5,31}$	38170 4	38177 1
$36_{7,29} - 36_{6,30}$	38202 5	38207 2
$37_{7,30} - 37_{6,31}$	37560 5	37567 0
$38_{7,31} - 38_{6,32}$	37500 0	37507 7
$39_{7,32} - 39_{6,33}$	38077 5	38086 0

± 2.5 MHz

4. Molecular Structure

The small values of the inertia defect for both species of the molecule seen from table 5 confirm the planarity of the molecule.

Table 5. Rotational constants, moments of inertia and quadrupole coupling constants of 3-chloropyridine

	Cl^{35}	Cl^{37}
A	5839 652±0 015 MHz	5839.575±0 024 MHz
B	1604 392±0 007 ,,	1558.825±0.005 ,,
C	1258 531±0 007 ,,	1230 299±0 005 ,,
κ	−0.8490058	−0 8574502
I_a	86.5687 amu Å^2	86 5698 amu Å^2
I_b	315 0919 ,,	324.3026 ,,
I_c	401 6834 ,,	410 9009 ,,
$\Delta = (I_c - I_a - I_b)$	0 0228 ,,	0 0285 ,,
χ_{aa}	−71 58 ±1 02 MHz	−57 35 ±0 95 MHz
χ_{bb}	37 63 ±1 45 ,,	31.11 ±1 34 ,,
χ_{cc}	33 95 ±1 02 ,,	26 24 ±0.95 ,,

Conversion factor = 505531 0 MHz amu Å^2

From the data presented in this work the co-ordinates of Cl in the inertial frame may be calculated The co-ordinates of the other atoms may be determined only after completion of the study of the microwave spectra of various species of the molecule incorporating isotopic substitution at the relevant atomic sites. Nevertheless, using the structure of pyridine as given by Bak *et al* (1958) and a C-Cl bond length of 1 71Å, it is possible to reproduce from such a model the experimentally observed value of I_a though the calculated value of I_a falls short of the experimental value by about 0.23 amu Å^2

Using the model for 3-chloropyridine described above, it is seen that the angle between the C-Cl bond axis and the principal axis a of the molecule is 1° 40′. The values of χ_{aa}, χ_{bb} and χ_{cc} given in Table 5 represent the hyperfine coupling constants in the directions of the principal axes of the molecule However, the values of the quadrupole coupling constants in the directions lying along and at right angles to the carbon-chlorine bond axis are of greater interest. To obtain the values of the hyperfine coupling constants along these directions, one simply transforms the hyperfine coupling tensor from the principal axes frame of the molecule to a frame defined by (a) an axis coincident with the C-Cl bond axis,

(*b*) an axis perpendicular to the first axis and lying in the plane of the molecule and (*c*) a third axis perpendicular to the other two axes. On carrying out such a transformation, one obtains a value of − 71 67 MHz for the hyperfine coupling constant along the carbon-chlorine bond axis This value compares favourably with the value of −70.476 MHz obtained by Bray *et al* (1958) for 3-chloropyridine in the solid state from nuclear quadrupole resonance studies The difference in values for the gas and solid phase studies is in conformity with expectation and is attributed to a small but significant increase in ionicity upon crystallization.

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